



Europäisches Patentamt
European Patent Office
Office européen des brevets



Publication number: **0 558 835 A1**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **92300777.7**

(22) Date of filing: **30.01.92**

(61) Int. Cl.⁵: **C10M 107/10, C10M 111/04, C10M 169/04, C10M 171/00, //(C10M111/04,101:02,101:04, 105:32,107:34,107:10), (C10M169/04,101:02,101:04, 105:32,107:34,107:10,133:12, 133:28),C10N30:20,C10N40:00**

(43) Date of publication of application:
08.09.93 Bulletin 93/36

(84) Designated Contracting States:
BE DE ES FR GB IT

(71) Applicant: **ETHYL S.A.**
Avenue Louise 523, (Boite 19)
B-1050 Bruxelles(BE)

(72) Inventor: **Platteau, Charles**
Chemin de Meslin, 3
B-7822 Ghislenghien(BE)

(74) Representative: **Collier, Jeremy Austin Grey et al**
J.A.Kemp & Co., 14 South Square, Gray's Inn
London WC1R 5LX (GB)

(54) **Biodegradable lubricants and functional fluids.**

(57) Certain unhydrogenated oligomers of 1-alkene hydrocarbons have been found to be substantially biodegradable upon exposure to microbiological agents of types widely available in the environment. Thus, in an operation wherein lubricating oil or functional fluid is released into the environment, there is provided for use as the lubricating oil or functional fluid a substantially biodegradable lubricating oil or functional fluid at least 10 percent by volume of which is composed of at least one substantially biodegradable unhydrogenated liquid hydrocarbon of lubricating viscosity formed by oligomerization of 1-alkene hydrocarbon having 8 to 20 carbon atoms in the molecule.

EP 0 558 835 A1

As is well known, there are many situations wherein oleaginous fluids are released into the environment. For example, lubricating oils utilized in the operation of out almost inevitably come in contact with the land and water surfaces of the earth. The same is true of oleaginous liquids used as carriers or diluents in agricultural sprays, such as herbicides and plant growth regulants. It is also commonplace for engine oils, transmission oils, gear box oils, etc., to leak onto pavement or ground surfaces and thus eventually find themselves in the natural environment. Another source of such releases to the environment involve rupture or leakages from high pressure hydraulic systems such as vehicular brake lines, hydraulic systems used in construction and earth moving equipment or military vehicles or equipment, and the like. Paper mill oils and compressor oils likewise find their way into the natural environment.

Unfortunately, formulated mineral oil lubricants and functional fluids can be harmful to the environment, since in most cases they are not acceptably biodegradable. Yet, in many cases, only hydrocarbonaceous fluids were deemed to possess the requisite combination of properties for the purposes at hand and to meet the economic parameters involved in the production and usage of such products. For example, synthetic ester oils and natural oils such as rapeseed oil possess shortcomings with respect to such properties as oxidative stability (especially at elevated use temperatures), hydrolytic stability, filterability, and demulsibility.

There is, therefore, a need for an efficacious way of reducing the extent and severity of such environmental abuse while at the same time providing lubricants and functional fluids possessing desirable physical properties within the confines of economic restraints. This invention is deemed to fulfill this need, confines of economic restraints. This invention is deemed to fulfill this need.

This invention involves, inter alia, the truly surprising discovery that certain unhydrogenated oligomers of 1-alkene hydrocarbons are substantially biodegradable upon exposure to microbiological agents of types widely available in the environment. Thus in operations wherein lubricating oils and functional fluids are released into the environment, accidentally or otherwise, the provision and the use of lubricants and functional fluids containing such unhydrogenated 1-olefin hydrocarbon oligomers can contribute materially to environmental protection. And moreover, such provision and such usage can be achieved without devastating consequences insofar as requisite performance properties and economic considerations are concerned.

Thus in accordance with one embodiment of this invention, in an operation wherein lubricating oil or functional fluid is released or likely to be released into the environment, there is provided the improvement which comprises providing for use as the lubricating oil or functional fluid a substantially biodegradable lubricating oil or functional fluid at least 10 percent by volume of which is composed of at least one substantially biodegradable unhydrogenated liquid hydrocarbon of lubricating viscosity formed by oligomerization of 1-alkene hydrocarbon having 6 to 20 carbon atoms in the molecule. In another embodiment of this invention, the improvement in such operation comprises using or utilizing as the lubricating oil or functional fluid in such operation a substantially biodegradable lubricating oil or functional fluid at least 10 percent by volume of which is composed of at least one substantially biodegradable unhydrogenated liquid hydrocarbon of lubricating viscosity formed by oligomerization of 1-alkene hydrocarbon having 6 to 20 carbon atoms in the molecule.

By "substantially biodegradable" in this specification and in the appended claims is meant that the oleaginous liquid in question has a biodegradability when tested and reported in accordance with test method CEC L-33-T-82 above 20%, preferably at least 30%, and more preferably at least 40%, and most preferably at least 50%. It is also to be noted that for the purposes of this invention the term "functional fluid" as used in the specification and claims includes solvents and/or carrier fluids (e.g., for agricultural sprays or formulations) as well as hydraulic fluids, quenching oils, cutting oils, machining oils, transformer oils, and the like.

Further embodiments of this invention include a substantially biodegradable lubricating oil or functional fluid composition which comprises at least 10% by volume of at least one substantially biodegradable unhydrogenated liquid hydrocarbon of lubricating viscosity formed by oligomerization of 1-alkene hydrocarbon having 6 to 20 carbon atoms in the molecule. In another of its forms, this invention relates to a substantially biodegradable lubricating oil or functional fluid composition of the type described above when in contact with at least one microbiological agent capable of causing biodegradation of at least a substantial portion of the substantially biodegradable unhydrogenated liquid hydrocarbon of which such lubricating oil or functional fluid composition is comprised. In this form of this invention, such microbiological agent can be in the earth or in a body of water.

Yet another embodiment of this invention concerns a method which comprises causing a lubricating oil or functional fluid composition of this invention to come in contact with at least one

microbiological agent capable of causing biodegradation of at least a substantial portion of the substantially biodegradable unhydrogenated liquid hydrocarbon content of such composition.

Other embodiments of this invention will be apparent from the ensuing description and appended claims.

Among the advantages of this invention are the surprising substantial biodegradability of the unhydrogenated 1-olefin oligomeric lubricants and functional fluids utilized in accordance with this invention, together with the combination of desirable properties which they possess. For example, the substantially biodegradable unhydrogenated poly- α -olefin lubricants and functional fluids of this invention possess in general better low temperature properties than comparable mineral oils. And as compared to synthetic ester oils and natural oils such as rapeseed oil, the substantially biodegradable lubricants and functional fluids of this invention generally possess better hydrolytic stability (e.g., in the ASTM hydrolytic stability test D 2619), superior filterability (e.g., in a wet filtration test), and better demulsibility (e.g., in the ASTM demulsibility test D 1401).

Not all unhydrogenated 1-alkene hydrocarbon liquid oligomers meet the substantially biodegradable requirements of this invention as above specified. Thus in any given situation recourse should be had to the simple expedient of subjecting the prospective unhydrogenated 1-alkene liquid oligomer to the CEC L-33-T-82 test procedure in the manner therein specified to determine the % biodegradability of the oligomer under consideration. Generally speaking, unhydrogenated liquid oligomers of linear 1-alkenes containing at least 50% dimer, trimer, and/or tetramer formed using a water or alcohol promoted Friedel-Crafts catalyst tend to possess the requisite biodegradability to be classified as substantially biodegradable and thus are preferred. Particularly preferred are liquid unhydrogenated oligomers of linear 1-alkenes containing at least 80 or 90% dimer and/or codimer species. The 1-alkenes used to form such oligomers should contain from 6 to 20 carbon and preferably from 8 to 16 carbon atoms in the molecule. In addition, such 1-alkenes should be linear (i.e., substantially free of branching and cyclization).

Methods for the production of such liquid oligomeric 1-alkene hydrocarbons are known and reported in the literature. See for example U. S. Pat. Nos. 3,763,244; 3,780,128; 4,172,855; and 4,218,330, omitting, of course the teachings therein concerning hydrogenation of the oligomers. As is well known, unhydrogenated oligomers of this type contain residual ethylenic unsaturation. Preferred oligomers are formed by use of a Friedel-Crafts

catalyst (especially boron trifluoride promoted with water or a C₁₋₂₀ alkanol) using oligomerization procedures such as are described in the foregoing U. S. patents.

Other catalyst systems which may also be used to form oligomers of 1-alkene hydrocarbons, which provide lubricants and functional fluids which may be substantially biodegradable, include Ziegler catalysts such as ethyl aluminum sesquichloride with titanium tetrachloride, aluminum alkyl catalysts, chromium oxide catalysts on silica or alumina supports and a system in which a boron trifluoride catalyst oligomerization is followed by treatment with an organic peroxide.

Mixtures or blends of such 1-alkene oligomers can also be used in the practice of this invention provided the overall blend possesses the requisite biodegradability as specified above.

It is also possible in accordance with this invention to utilize blends of one or more sufficiently biodegradable liquid unhydrogenated 1-alkene oligomers in combination with other oleaginous materials which are themselves sufficiently biodegradable such that the resultant blend meets the biodegradability requirement of this invention, and provided further that the resultant blend possesses the requisite compatibility, stability and performance criteria for the use for which the blend is designed, formulated, and provided.

Illustrative non-oligomeric oils and fluids of lubricating viscosity which can be used in formulating substantially biodegradable lubricating oil and/or functional fluid blends pursuant to this invention, include synthetic esters such as mixed C₉ and C₁₁ dialkylphthalates (e.g., ICI Emkarate 911P ester oil), trimethylol propane trioleate, di-(isotridecyl)-adipate (e.g., BASF Glissolfluid A13), pentaerythritol tetraheptanoate and the like; substantially biodegradable liquid hydrogenated 1-alkene oligomers such as ETHYLFO 162, 164 and 166 poly-alpha-olefin oils and blends thereof (Ethyl Corporation; Ethyl S.A.; Ethyl Canada Limited); and liquid natural fatty oils and esters such as castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil, jojoba oil, and the like. Such natural fatty oils may be partially or fully hydrogenated, if desired. Here again, the only requirements are that the resultant blend be substantially biodegradable within the meaning specified above and that the blend have the requisite properties for the intended use or uses therefor.

It is also possible to include small amounts of mineral oils in blends with one or more substantially biodegradable linear 1-alkene hydrocarbon oligomers, and such blends may in turn contain one or more other base oils (synthetic ester,

polyalkylene glycol, hydrogenated poly-alpha-olefin oil, natural fatty oil or ester, etc.), provided that the overall blend is itself substantially biodegradable. The amount of mineral oil which can be present in the foregoing blends will depend in large measure upon the structural and molecular characteristics of the mineral oil, such as the amount of methyl-branched and cyclic species present, configurations which resist biodegradation. Accordingly in any given situation recourse should be had to the CEC L-33-T-72 test procedure to insure that the proposed amount of the proposed mineral oil in the proposed overall blend does not prevent the overall blend from being substantially biodegradable.

Conventional amounts of conventional additives typically used in lubricating oils and/or in functional fluids can be utilized in the liquid unhydrogenated 1-alkene hydrocarbon oligomer-containing compositions of this invention, provided of course that the additives as used are compatible with each other and are sufficiently soluble in the base oil at the desired concentrations to provide a homogenous solution at ambient temperatures. Examples of such additives, although well known to those skilled in the art, are given hereinafter. It is worth noting that such additives need not in and of themselves be biodegradable. The only requirement is that the concentrations employed -- which are normally relatively low -- in the base oil should not prevent the finished lubricant or functional fluid from remaining substantially biodegradable.

Thus, in one of its preferred embodiments this invention provides a substantially biodegradable lubricating composition comprising:

- (a) an unsaturated poly- α -olefin having a viscosity of 11-1,000 mm²/s at 100 °C;
- (b) an ester having a viscosity of 11-1,000 mm²/s at 100 °C; and
- (c) an additive package comprising at least one additive selected from the group consisting of dispersants, oxidation inhibitors, corrosion inhibitors, metal passivators, antirust agents, antiwear agents, foam inhibitors, extreme pressure agents, tackiness agents and friction modifier agents.

Still another embodiment of this invention provides a substantially biodegradable lubricating composition comprising:

- (a) an unsaturated poly- α -olefin having a viscosity of 11-1,000 mm²/s at 100 °C;
- (b) a saturated and/or unsaturated synthetic hydrocarbon having a viscosity of 1-10 mm²/s at 100 °C;
- (c) an ester having a viscosity of 11-1,000 mm²/s at 100 °C; and
- (d) an additive package comprising at least one additive selected from the group consisting of dispersants, oxidation inhibitors, corrosion inhibi-

tors, metal passivators, antirust agents, antiwear agents, foam inhibitors, extreme pressure agents, tackiness agents and friction modifier agents.

To still further protect the environment, this invention provides in accordance with preferred embodiments thereof, novel compositions which facilitate the detection of leakage and other excessive releases of lubricant and/or functional fluid to the environment. Thus to the extent, if any, that the lubricant or functional fluid composition is not biodegradable, early detection of such leakage or excessive release thereof to the environment enables prompt remedial action to be taken to arrest further leakage or excessive release to the environment.

In accordance with such preferred embodiments there are provided substantially biodegradable lubricating oil or functional fluid compositions which comprise a major proportion of an oleaginous fluid containing a small visually-perceptible chromophoric quantity of an oil-soluble chromophoric substance. Such oleaginous fluid comprises by volume at least 10 percent, preferably at least 25 percent, more preferably at least 50 percent, still more preferably at least 75 percent, and most preferably 90 percent or more of at least one substantially biodegradable unhydrogenated liquid hydrocarbon of lubricating viscosity formed by oligomerization of 1-alkene hydrocarbon having 6 to 20 carbon atoms in the molecule, and hydrogenation of oligomer so formed. Preferably, the chromophoric substance employed has a maximum absorption wavelength within the range of 300 to 650 millimicrons. Typical, but preferred, chromophoric substances have maximum absorption wavelengths respectively of 400, 420, 515, 518, and 640 millimicrons. A particularly preferred chromophoric substance is comprised of a mixture of two chromophoric compounds, one having a maximum absorption wavelength of about 420 millimicrons and the other a maximum absorption wavelength of about 640 millimicrons, whereby the product has a green coloration.

The following examples, in which parts and percentages of components are by weight, illustrate but do not limit, and should not be construed as limiting, the practice of this invention. The biodegradation results using the CEC L-33-T-82 test procedure are expressed with reference to a standard of 90% biodegradability for di(isotridecyl)-adipate and 20% biodegradability for white mineral oil. In the case of the OECD 301B Modified Stürm test method, the standard reference is 90% biodegradability for sodium benzoate.

EXAMPLE 1

An unhydrogenated oligomer of 1-decene having a kinematic viscosity at 100 °C of 3.5 cSt was placed in contact with a bacterial inoculum from a sewage plant pursuant to test method CEC L-33-T-82. Upon completion of the test in accordance with such test method, the lubricant was found to have a biodegradation of about 48%.

EXAMPLE 2

An unhydrogenated 1-dodecene dimer was found to have a biodegradation of approximately 41% when subjected to the CEC L-33-T-82 biodegradability test procedure.

EXAMPLE 3

An unhydrogenated mixture of dimers formed from a mixture of 1-tetradecene and 1-hexadecene exhibited a biodegradation of about 57% in the CEC L-33-T-82 biodegradability test procedure.

EXAMPLE 4

A blend was formed from 29.3 parts of Ketjenlube 165 synthetic lubricating oil (Akzo Chemical Company) and 67.7 parts of a fraction of unhydrogenated 1-decene oligomer having a kinematic viscosity of 3.5 cSt at 100 °C. An experimental ashless hydraulic fluid additive pack was blended into this base oil fluid to a concentration of 0.6%. The resultant wear-inhibited hydraulic fluid composition of ISO viscosity grade 32 exhibited a biodegradation of about 67% in the CEC L-33-T-82 biodegradability test procedure.

EXAMPLE 5

A hydraulic fluid was formed by blending an experimental ashless hydraulic fluid additive pack to a concentration of 1.0% in an unhydrogenated 1-decene oligomer fraction described in Example 4. On subjecting this ashless wear-inhibited hydraulic fluid to the CEC L-33-T-82 biodegradability test procedure, the fluid was found to have a biodegradation of about 81%.

EXAMPLE 6

The procedure of Example 4 was repeated using 40 parts of Ketjenlube 165 synthetic lubricating oil and 59 parts of the 3.5 cSt unhydrogenated 1-decene oligomer as the base fluid. The wear-inhibited ashless hydraulic fluid containing 1.0% of the experimental ashless hydraulic fluid antiwear package was of ISO viscosity grade 46 and had a

biodegradation in the CEC L-33-T-82 test procedure of about 78%. A duplicate determination showed the blend to give a biodegradation of about 55%.

EXAMPLE 7

Six chromophoric lubricant and functional fluid base oil compositions of this invention are formed by blending with the synthetic lubricating oils as described in Examples 1 through 6, 0.01% of a methyl derivative of azobenzene-4-azo-2-naphthol having a maximum absorption wavelength of 518 millimicrons and an approximate pour point of -26 °C (C.I. Solvent Red 164). Leakage or spillage of these substantially biodegradable lubricant compositions is readily perceived by the naked eye.

EXAMPLE 8

Six chromophoric lubricant and functional fluid base oil compositions of this invention are formed by blending with the synthetic lubricating oils as described in Examples 1 through 6, 0.02% of a mixture of p-diethylaminoazobenzene having a maximum absorption wavelength of 420 millimicrons and 1,4-diisopropylaminoanthraquinone having a maximum absorption wavelength of 640 millimicrons and an approximate pour point of -46 °C. Leakage or spillage of these substantially biodegradable lubricant compositions is readily perceived visually.

EXAMPLE 9

Six chromophoric lubricant and functional fluid base oil compositions of this invention are formed by blending with the synthetic lubricating oils as described in Examples 1 through 6, 0.025% of benzene-azo-2-naphthol having a maximum absorption wavelength of 400 millimicrons and an approximate pour point of -23 °C. Leakage or spillage of these substantially biodegradable lubricant compositions is readily perceived visually.

EXAMPLE 10

A functional fluid is formed by blending together equal volumes of the unhydrogenated poly- α -olefin synthetic lubricating oil as described in Example 1 and rapeseed oil. This functional fluid is provided for use as a hydraulic fluid and solvent for herbicides. When the functional fluid is released to the natural environment, it is biodegraded to a greater extent than a conventional mineral oil of the same viscosity.

EXAMPLE 11

Chromophoric substantially biodegradable base oil compositions of this invention are formed by dissolving the combination of Hoechst Fat Blue B at a concentration equivalent to 0.04g/400mL and Hoechst Fat Yellow 3 G at a concentration equivalent to 0.10 g/400mL into the fluid compositions described in Examples 1 through 6. When in contact with microbiological agents in the natural environment (soil or water) such base oils are substantially biodegraded into innocuous materials.

EXAMPLE 12

A blend was formed composed of 29.5% of Ketjenlube 165 synthetic ester lubricating oil (Akzo Chemical Company), 69.5% of a fraction of unhydrogenated 1-decene oligomer having a kinematic viscosity of 3.5 cSt at 100 °C and 1.0% of an ashless additive package containing antioxidant and antiwear/extreme pressure agents. The wear-inhibited ashless hydraulic fluid was of ISO viscosity grade 32 and exhibited a biodegradation in the CEC L-33-T-82 test procedure averaging about 72% in triplicate determinations.

EXAMPLE 13

A blend was formed composed of 32.0% of Ketjenlube 1579 synthetic lubricating oil (Akzo Chemical Company), 67.0% of a fraction of unhydrogenated 1-decene oligomer having a kinematic viscosity of 3.5 cSt at 100 °C and 1.0% of an ashless additive package containing antioxidant and antiwear/extreme pressure agents. The wear-inhibited ashless hydraulic fluid was of ISO viscosity grade 32 and exhibited a biodegradation in the CEC L-33-T-82 test procedure of about 35%.

EXAMPLE 14

The procedure of Example 13 was repeated except that Ketjenlube 1580 was used in place of Ketjenlube 1579. In all other respects the composition was identical. This ISO viscosity grade 32 blend exhibited a biodegradation in the CEC L-33-T-82 test procedure of about 32%.

EXAMPLE 15

A blend was formed from 42 parts of Ketjenlube 1579 synthetic lubricating oil (Akzo Chemical Company), and 57 parts of a fraction of unhydrogenated 1-decene oligomer having a kinematic viscosity of 3.5 cSt at 100 °C containing 1.0% of an ashless additive package containing antioxidant and antiwear/extreme pressure agents.

The wear-inhibited ashless hydraulic fluid was of ISO viscosity grade 46 and exhibited a biodegradation in the CEC L-33-T-82 test procedure of about 44%.

EXAMPLE 16

A blend was formed from 45 parts of Ketjenlube 1580 synthetic lubricating oil (Akzo Chemical Company), and 54 parts of a fraction of unhydrogenated 1-decene oligomer having a kinematic viscosity of 3.5 cSt at 100 °C containing 1.0% of an ashless additive package containing antioxidant and antiwear/extreme pressure agents. The wear-inhibited ashless hydraulic fluid was of ISO viscosity grade 46 and exhibited a biodegradation in the CEC L-33-T-82 test procedure of about 24%.

EXAMPLE 17

An unhydrogenated oligomer of 1-decene having a kinematic viscosity at 100 °C of 2.0 cSt was placed in contact with a bacterial inoculum from a sewage plant pursuant to test method CEC L-33-T-82. Upon completion of the test in accordance with such test method, the lubricant was found to have a biodegradation of about 82%. When subjected to the Modified Stürm procedure (OECD 301B), the biodegradation was 42%.

The substantially biodegradable lubricants and functional fluids of this invention can be employed in a wide variety of applications. For example they can be employed as base oils for crankcase lubricants, automotive gear lubricants, transmission oils, hydraulic oils, paper mill oils, compressor oils, outboard motor lubricants (2-cycle oils), chain saw lubricants, carriers for herbicides and plant growth regulants, and for other similar uses. When in the course of such usage the substantially biodegradable base oils of this invention are released into the environment, accidentally or otherwise, and come in contact with microbiological agents in the natural environment, the oils are substantially biodegraded and thus such oils are much less offensive to the environment than substantially non-biodegradable base oils.

Well known additives which may be included in the compositions of this invention include the zinc dialkyl (C_3-C_{10}), dicycloalkyl (C_5-C_{20}), and/or diaryl (C_6-C_{20}) dithiophosphate wear inhibitors, generally present in amounts of about 0.5 to 5 weight percent. Useful detergents include the oil-soluble normal basic or overbased metal, e.g., calcium, magnesium, barium, etc., salts of petroleum naphthenic acids, petroleum sulfonic acids, alkyl benzene sulfonic acids, oil-soluble fatty acids, alkyl salicylic acids, sulfurized or unsulfurized alkyl phenates, and

hydrolyzed or unhydrolyzed phosphosulfurized polyolefins. Gasoline engine crankcase lubricants typically contain, for example, from 0.5 to 5 weight percent of one or more detergent additives. Diesel engine crankcase oils may contain substantially higher levels of detergent additives. Preferred detergents are the calcium and magnesium normal or overbased phenates, sulfurized phenates or sulfonates.

Pour point depressants which may be present in amounts of from 0.01 to 2 weight percent include wax alkylated aromatic hydrocarbons, olefin polymers and copolymers, and acrylate and methacrylate polymers and copolymers.

Viscosity index improvers, the concentrations of which may vary in the lubricants from 0.2 to 15 weight percent, (preferably from about 0.5 to about 5 weight percent) depending on the viscosity grade required, include hydrocarbon polymers grafted with, for example, nitrogen-containing monomers, olefin polymers such as polybutene, ethylene-propylene copolymers, unhydrogenated polymers and copolymers and terpolymers of styrene with isoprene and/or butadiene, polymers of alkyl acrylates or alkyl methacrylates, copolymers of alkyl methacrylates with N-vinyl pyrrolidone or dimethylaminoalkyl methacrylate, post-grafted polymers of ethylene-propylene with an active monomer such as maleic anhydride which may be further reacted with an alcohol or an alkylene polyamine, styrene/maleic anhydride polymers post-treated with alcohols and amines, etc.

Antiwear activity can be provided by about 0.01 to 2 weight percent in the oil of the aforementioned metal dihydrocarbyl dithiophosphates and the corresponding precursor esters, phosphosulfurized pinenes, sulfurized olefins and hydrocarbons, sulfurized fatty esters and alkyl polysulphides. Preferred are the zinc dihydrocarbyl dithiophosphates which are salts of dihydrocarbyl esters of dithiophosphoric acids.

Other additives include effective amounts of friction modifiers or fuel economy additives such as the alkyl phosphonates as disclosed in U.S. 4,356,097, aliphatic hydrocarbyl substituted succinimides as disclosed in EPO 0020037, dimer acid esters, as disclosed in U.S. 4,105,571, oleamide, etc., which are present in the oil in amounts of 0.1 to 5 weight percent. Glycerol oleates are another example of fuel economy additives and these are usually present in very small amounts, such as 0.05 to 0.2 weight percent based on the weight of the formulated oil.

Antioxidants or thermal stabilizers which may be used include hindered phenols, methylene-bridged polyphenols, aromatic amine antioxidants, sulfurized phenols, alkyl phenothiazines, substituted triazines and ureas, and copper compounds

such as copper naphthenate and copper oleate, among others. Phenolic antioxidants are preferred.

Detergents and dispersants can also be used in the compositions of this invention, again subject to the proviso that the material used not interfere with the substantial biodegradability of the overall composition. Typical dispersants include the reaction products of hydrocarbyl-substituted acylating agents such as alkenyl- or alkyl- substituted succinic acid or anhydride with amines, phenols, alcohols, aminoalcohols, or basic inorganic materials. Polyisobutenyl succinimides of alkylene polyamines are preferred dispersants of this type.

Numerous references describe such materials and their use. See for example U.S. Pat. Nos. 3,163,603; 3,184,474; 3,215,707; 3,219,666; 3,271,310; 3,272,746; 3,281,357; 3,306,908; 3,311,558; 3,316,177; 3,340,281; 3,341,542; 3,346,493; 3,351,552; 3,381,022; 3,399,141; 3,415,750; 3,433,744; 3,444,170; 3,448,048; 3,448,049; 3,451,933; 3,454,607; 3,467,668; 3,501,405; 3,522,179; 3,541,012; 3,542,680; 3,543,678; 3,567,637; 3,574,101; 3,576,743; 3,630,904; 3,632,510; 3,632,511; 3,697,428; 3,725,441; 4,234,435; Re 26,433.

Also useful are products formed by reacting aliphatic or alicyclic halides with amines as described, for example, in U.S. 3, 275,554; 3,438,757; 3,454,555; and 3,565,804.

Mannich reaction products are another type of useful ashless dispersant. Dispersants of this type are described for example, in U.S. Pat. Nos. 2,459,112; 2,962,442; 2,984,550; 3,036,003; 3,166,516; 3,236,770; 3,355,270; 3,368,972; 3,413,347; 3,442,808; 3,448,047; 3,454,497; 3,459,661; 3,461,172; 3,493,520; 3,539,633; 3,558,743; 3,588,629; 3,591,598; 3,600,372; 3,634,515; 3,649,229; 3,697,574; 3,725,277; 3,725,480; 3,726,882; and 3,980,569.

Products formed by post-treating the various types of dispersants referred to above with suitable reactants are also useful. Products of this type are described, for example, in U.S. Pat. Nos. 3,036,003; 3,087,936; 3,200,107; 3,216,936; 3,254,025; 3,256,185; 3,278,550; 3,280,234; 3,281,428; 3,282,955; 3,312,619; 3,366,569; 3,367,943; 3,373,111; 3,403,102; 3,442,808; 3,455,831; 3,455,832; 3,493,520; 3,502,677; 3,513,093; 3,533,945; 3,539,633; 3,573,010; 3,579,450; 3,591,598; 3,600,372; 3,639,242; 3,649,229; 3,649,659; 3,658,836; 3,697,574; 3,702,757; 3,703,536; 3,704,308; 3,708,422; and 4,857,214.

Polymeric dispersants such as interpolymers of decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides, and poly(oxyethylene) acrylates. Typical

materials of this general type are described, for example in U.S. Pat. Nos. 3,329,658; 3,449,250; 3,519,565; 3,666,730; 3,687,849; and 3,702,300.

Extreme pressure agents which also have corrosion-inhibiting and oxidation-inhibiting properties can also be used. These include chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulphides and polysulphides such as benzyl disulphide, bis(chlorobenzyl)disulphide, dibutyl tetrasulphide, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, and sulfurized terpene; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulphide with turpentine or methyl oleate, phosphorus esters including principally dihydrocarbon and trihydrocarbon phosphites such as dibutyl phosphite, diheptyl phosphite, dicyclohexyl phosphite, pentylphenyl phosphite, dipentylphenyl phosphite, tridecyl phosphite, distearyl phosphite, dimethyl naphthyl phosphite, oleyl 4-pentylphenyl phosphite, polypropylene (molecular weight 500)-substituted phenyl phosphite, diisobutyl-substituted phenyl phosphite; metal thiocarbamates, such as zinc dioctyldithiocarbamate, and barium heptylphenyl dithiocarbamate; Group II metal phosphorodithioates such as zinc dicyclohexylphosphorodithioates, zinc dioctylphosphorodithioate, barium di(heptylphenyl)phosphorodithioates, cadmium dinonylphosphorodithioates, and the zinc salt of a phosphorodithioc acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol.

Many of the above-mentioned auxiliary extreme pressure agents and corrosion-oxidation inhibitors also serve as antiwear agents. Zinc dialkylphosphorodithioates are a well known example.

Tackiness additives such as HITEC® 151 Additive (Ethyl Corporation; Ethyl S.A.; Ethyl Canada Limited) are also useful.

Other well known components such as rust inhibitors, wax modifiers, foam inhibitors, copper passivators, sulfur scavengers, seal swell agents, color stabilizers, and like materials can be included in the compositions of this invention, provided of course that they are compatible with the base lubricant and the other component or components being employed.

Claims

1. A substantially biodegradable lubricating oil or functional fluid composition which comprises at least 10% by volume of at least one substantially biodegradable unhydrogenated liquid hydrocarbon of lubricating viscosity formed by oligomerization of 1-alkene hydrocarbon having 6 to 20 carbon atoms in the molecule.

2. A composition according to Claim 1 wherein said substantially biodegradable lubricating oil or functional fluid contains at least 50 percent by volume of said at least one substantially biodegradable unhydrogenated liquid hydrocarbon.
3. A composition according to Claim 1 wherein said substantially biodegradable lubricating oil or functional fluid contains at least 90 percent by volume of said at least one substantially biodegradable unhydrogenated liquid hydrocarbon.
4. A composition according to any of Claims 1 through 3 wherein said at least one substantially biodegradable liquid hydrocarbon contains a small visually-perceptible chromophoric quantity of at least one oil-soluble chromophoric substance.
5. A composition according to Claim 4 wherein said at least one oil-soluble chromophoric substance has a maximum absorption wavelength in the range of 300 to 700 millimicrons.
6. A composition according to Claim 5 wherein said at least one oil-soluble chromophoric substance comprises a combination of two such substances, one of which has a maximum absorption wavelength of about 420 millimicrons and the other of which has a maximum absorption wavelength of about 640 millimicrons whereby the product has a green coloration.
7. A method of operation involving the use of a lubricating oil or functional fluid wherein the said lubricating oil or functional fluid is as claimed in any one of claims 1 to 6.
8. A method according to Claim 7 in which said operation comprises the operation of a chain saw, an outboard motor, a hydraulic system, a motor vehicle, or earth-moving equipment.
9. A method according to claim 7 or 8 wherein the operation takes place in an environment in which use of non-biodegradable materials is to be avoided.
10. A method according to claim 7 or 8 wherein at least part of said oil or fluid is released into the environment and comes into contact with at least one microbiological agent capable of causing biodegradation of at least a substantial portion of said substantially biodegradable liquid hydrocarbon.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 0777

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	EP-A-0 468 109 (ETHYL PETROLEUM ADDITIVES) * claims 1,2,6-10 * * column 8, line 25 - line 37 * —	1-10	C10M107/10 C10M111/04 C10M169/04 C10M171/00
Y	EP-A-0 467 345 (ETHYL CORPORATION) * claim 7 * —	1-10	/(C10M111/04, 101:02, 101:04, 105:32, 107:34, 107:10)
X	EP-A-0 103 884 (STAUFFER CHEMICAL COMPANY) * claims 1-3,5 * —	1,7,8	(C10M169:04, 101:02, 101:04, 105:32, 107:34, 107:10, 133:12, 133:28) (C10N30:20) (C10N40:00)
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C10M
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31 AUGUST 1992	Examiner HILGENA K.J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	

EP-0 FORM 1500 (04/83) (P.0001)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☒ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.